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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Organosilicon Compositions

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the States of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel organosilicon compositions, particularly to novel organosilicon polyoxyalkylene organic surfactant compositions useful in aqueous systems.

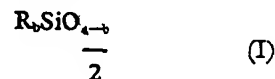
Surfactants, or surface-active agents, have been previously defined in the art as solutes which possess the property of altering the surface or interfacial characteristics of their solutions to an unusual extent.

It has now been found that the surface tension of an aqueous solution of organic surfactant can be lowered to a marked extent and its surface active properties thereby appreciably increased when an organosiloxane-oxyalkylene block copolymer as hereinafter described is present.

The organosiloxane-oxyalkylene block copolymer should be somewhat water-soluble or have an affinity for water in order to aid in the surfactant activity. These block copolymers are especially useful in this respect since unlike most water soluble organosilicon compounds, they do not hydrolyze upon standing in water solution. Undesirable by-product contamination is thus avoided and surfactant activity is maintained at highest effectiveness.

According to the present invention therefore there is provided a composition suitable for use in reducing the surface tension of aqueous solutions which comprises (1) an organic surfactant and (2) an organo-siloxane-oxyalkylene block copolymer comprising (a) at least one

siloxane block containing at least two siloxane units represented by the formula:



wherein each R is a monovalent hydrocarbon radical, a halogen-substituted monovalent hydrocarbon radical or a divalent hydrocarbon radical and preferably each R contains from 1 to 20 carbon atoms, and b is 1, 2 or 3, said siloxane block containing at least one of said siloxane units wherein at least one R radical is a divalent hydrocarbon radical, and (b) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R'O—, wherein R' is an alkylene radical preferably containing from 2 to 10 carbon atoms, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon radical.

The organosiloxane-oxyalkylene copolymers useful in the compositions of this invention are of the class that are known as "block" copolymers. Block copolymers are composed of at least two sections or blocks at least one section or block composed of one type of recurring units (e.g., siloxane units as in the copolymers useful in this invention) and at least one other section or block composed of a different type of recurring groups (e.g. oxyalkylene groups as in the copolymers useful in this invention). Block copolymers can have linear, cyclic, branched or cross-linked structures.

The radicals represented by R can be the same or different in any given siloxane unit or throughout the siloxane block, and the value of b in the various siloxane units in the siloxane block can be the same or different. The divalent hydrocarbon radicals represented by R link the siloxane block to the oxyalkylene

aliphatic radicals (e.g., the cyclohexyl and the cyclopentyl radicals), the aryl radicals (e.g. the phenyl, tolyl, xylyl, naphthyl and terphenyl radicals), the aralkyl radicals, e.g., the benzyl and betaphenylethyl radicals), the unsaturated linear aliphatic radicals (e.g., the vinyl, allyl and hexenyl radicals) and the unsaturated cycloaliphatic radicals (e.g. the cyclohexenyl radical).

10 Illustrative of the halogen-substituted monovalent hydrocarbon radicals represented by G are the chloromethyl, trichloroethyl, perfluorovinyl, para - bromobenzyl, iodophenyl, alpha-chloro - beta - phenylethyl, para - chlorotolyl and bromocyclohexyl radicals.

15 Preferably, the G and G' radicals [included in the definition of R in formulae (1) and (1-a) above] contain from one to twenty carbon atoms and the G'' radicals [included in the definition of R' in formula (2) above] contain from two to ten carbon atoms. When the G''' radical is a monovalent hydrocarbon radical free of aliphatic unsaturation it preferably contains from one to twelve carbon atoms.

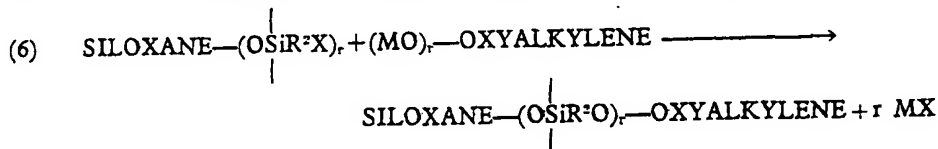
20 Illustrative of the divalent hydrocarbon radicals represented by G' in formulae (3), (4) and (5) are the alkylene radicals (e.g., the methylene, ethylene, 1,3-propylene, 1,4-butylene, 1,12-dodecylene and 1,20-eicosylene radicals), the arylene radicals (e.g., the phenylene radical) and the alkarylene radicals (e.g., the phenylethylene radicals). In formulae (3), 30 (4) and (5), G' is preferably an alkylene

radical containing at least two carbon atoms.

Illustrative of the alkylene radicals containing at least two carbon atoms represented by G'' in formulae (3), (4) and (5) are the ethylene, 1,2-propylene, 1,3-propylene, 1,6-hexylene, 2-ethylhexylene-1,6 and 1,12-dodecylene radicals.

40 Illustrative of the radicals represented by G''' in formulae (3), (4) and (5) are the saturated linear or branched chain aliphatic hydrocarbon radicals (e.g., the methyl, ethyl, propyl, N-butyl, tert.-butyl and decyl radicals), the saturated cycloaliphatic hydrocarbon radicals (e.g., the cyclopentyl and cyclohexyl radical, the aryl hydrocarbon radicals (e.g., the phenyl, tolyl, naphthyl and xylyl radicals), and the aralkyl hydrocarbon radicals (e.g., the benzyl and betaphenylethyl radicals).

50 The siloxane-oxyalkylene block copolymers useful in the compositions of this invention can be prepared by several convenient methods. For example, the copolymers useful in this invention can be produced by a process that involves forming a mixture of a siloxane polymer containing a silicon-bonded, radical and an alkali metal salt of an oxyalkylene polymer and heating the mixture to a temperature sufficiently elevated to cause the siloxane polymer and the salt to react to produce the copolymer. This process is referred to herein as the "metathesis process" and it involves a metathesis reaction that can be illustrated by the following equation:

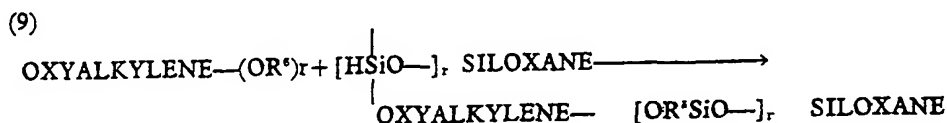


70 wherein R² is a divalent hydrocarbon radical, r is an integer that has a value of at least 1 and preferably 1 to 4, X is a halogen atom, M is an alkali metal, SILOXANE denotes a siloxane block and OXYALKYLENE denotes an oxyalkylene block.

75 The copolymers useful in this invention can also be produced by another process (termed the "addition process") that involves forming a mixture of a siloxane polymer containing a

hydrogen-siloxy group (i.e., a HSiO-group),

80 an oxyalkylene polymer containing an alkenyloxy chain terminating radical and a platinum catalyst and heating the mixture to a temperature sufficiently elevated to cause the siloxane polymer and the oxyalkylene polymer to react to produce the copolymer. The latter-mentioned reaction is an addition reaction that can be illustrated by the following equation:



90 wherein OXYALKYLENE, SILOXANE and r have the meaning defined for formula (6), OR^s is an alkenyloxy radical (such as, the vinyloxy and the allyloxy radicals) and R^s is an alkylene radical containing at least two successive carbon atoms. The addition process is applicable to the production of those

95 copolymers of this invention containing a siloxane block that is linked to an oxyalkylene block by an alkylene radical that has at least two successive carbon atoms (e.g., an ethylene, 1,2-propylene or 1,2-butylene radical).

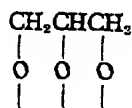
When the polysiloxane-oxyalkylene block copolymer contains silicon-bonded hydrogen 100

that is attributable to the siloxane blocks can be as high as 50,000 or greater.

Water-solubility of the copolymer is enhanced when R' contains less than three carbon atoms. It is therefore important that at least one $-\text{C}_2\text{H}_4\text{O}-$ group be present in the copolymer for it to be at least partially water-soluble. Illustrative of the oxyalkylene groups that are represented by formula (2) are the oxyethylene, oxy - 1,2 - propylene, oxy - 1,3 - propylene, oxy - 2,2 - dimethyl - 1,3 - propylene, and oxy - 1,10 - decylene groups.

The oxyalkylene blocks in the copolymers useful in the compositions of this invention can contain one or more of the various types of oxyalkylene groups represented by formula (2). By way of illustration, the oxyalkylene blocks can contain only oxyethylene groups or only oxypropylene groups or both oxyethylene and oxypropylene groups, or other combinations of the various types of oxyalkylene groups or only oxypropylene groups or both oxyethylene and oxypropylene groups, or other combinations of the various types of oxyalkylene groups represented by formula (2).

The oxyalkylene blocks in the copolymers useful in the compositions of this invention can contain organic chain-terminating groups. By way of illustration, the oxyalkylene block can contain such chain-terminating groups as the hydroxy group, the aryloxy radical (such as, the phenoxy radical), the alkoxy radical (such as, the methoxy, ethoxy, propoxy and butoxy radical) and alkenyloxy radical (such as, the vinyloxy and the allyloxy radicals). Also, a single group can serve as a chain-terminating group for more than one oxyalkylene block. For example the glyceroxy group,



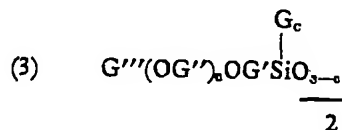
can serve as a chain-terminating group for three oxyalkylene chains.

Preferably, each oxyalkylene block contains at least four groups, represented by the formula $-\text{R}'\text{O}-$ in which R' has the meaning given above. That part of the average molecular weight of the copolymer that is attributable to the oxyalkylene blocks can vary from 88 for $(\text{C}_2\text{H}_4\text{O})_2$ to 50,000 or greater.

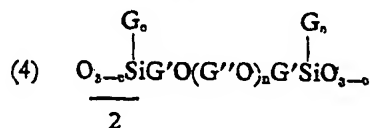
The block copolymers useful in the compositions of this invention may contain siloxane blocks and oxyalkylene blocks in any relative amount. In order to possess desirable properties, the copolymer preferably contains from 5 to 95 parts by weight of siloxane blocks and from 5 to 95 parts by weight of oxyalkylene blocks per 100 parts by weight of the copolymer. More preferably, the copolymers contains 5 to 50 parts by weight of the siloxane blocks and from 50 to 95 parts by weight of the oxyalkylene blocks per 100 parts by weight of the copolymer.

The block copolymers useful in the compositions of this invention may contain more than one of each of the blocks and the blocks can be arranged in various configurations such, as linear, cyclic or branched configurations. By way of illustration, the following classes of compounds are among the siloxane-oxyalkylene block copolymers useful in the formulations of this invention:

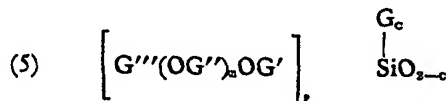
(A) Copolymers that contain at least one unit that is represented by the formula:



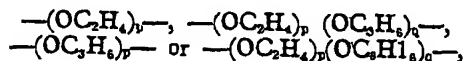
(B) Copolymers that contain at least one unit that is represented by the formula:



(C) Copolymers that contain at least one unit that is represented by the formula:



In the above formulae (3), (4) and (5), G is a monovalent hydrocarbon radical or a halogen-substituted monovalent hydrocarbon radical, G' is a divalent hydrocarbon radical, G'' is an alkylene radical containing at least two carbon atoms, G''' is a hydrogen atom or a monovalent hydrocarbon radical free of aliphatic unsaturation, n is an integer having a value of at least two, and c is 0, 1 or 2 in formulae (3) and (4) and 0, or 1 in formula (5). In formulae (3), (4) and (5), G can represent the same or different radicals, n preferably has a value of from two to 30 and G'' can represent the same or different radicals, i.e. the group $(\text{OG}')_n$ can represent, for example, the groups:



where p and q are integers having a value of at least one.

The monovalent hydrocarbon radicals and halogen-substituted monovalent hydrocarbon radicals represented by G in formulas (3), (4) and (5) can be saturated or olefinically unsaturated, or can contain benzenoid unsaturation. Illustrative of the monovalent hydrocarbon radicals represented by G are the linear aliphatic radicals (e.g. the methyl, ethyl, decyl, octadecyl and eicosyl radicals), the cyclo-

5 sulphate, triethanolamine ammonium lauryl sulphate, sodium 2-ethylhexanol sulphate, sodium cetyl sulphate, ammonium nonylphenyl polyglycol ether sulphate, sodium oleyl sulphate, ammonium nonylphenoltetraethoxy sulphate, sodium nonylphenoltetraethoxy sulphate, triethanolamine nonylphenoltetraethoxy sulphate, monoethanolamine lauryl ether sulphate, magnesium lauryl ether sulphate; and polyethylene glycol dodecylthioether.

10 Cationic surfactants useful in the present invention can be amine salts, such as, dodecyl dimethyl amine acetate, cetyl dimethyl amine oxide, cetyl pyridinium chloride, stearyl dimethyl benzyl ammonium chloride, lauryl pyridinium chloride; heterocyclic amines, such as, N - cetyl - piperidine and N - stearyl-piperidine; and sulphated cresylic acid.

15 Nonionic surfactants can be fatty substituted alcohols, such as, acetylated lanolin alcohols, nonylphenoxy polyethylene ethanol, octylphenoxy-poly (ethylenoxy)ethanol, nonylphenolpolyglycol ether alcohol, octylphenolpolyglycol ether alcohol, sorbitan mono-oleate, polyoxyethylene sorbitan tristearate; amine esters of fatty carboxylic acids, such as, lauric acid monoethanolamide, lauric acid isopropanolamide, lauric acid diethanolamide, myristic diethanolamide; N-fatty trimethylene diamine; and polyethylene glycol tert-dodecyl thioether.

20 Amphoteric surfactants can be lecithin, sodium N-coco beta - aminopropionate, disodium N-tallow beta-amino dipropionate N-lauryl beta-aminopropionic acid, cetyl betaine, cetylaminooacetic acid, sodium N-methyltaurate, and ethylene cycloimido - 1 - lauryl - 2 - hydroxy - 2 - ethylene sodium alcoholate-2 - methylene sodium carboxylate.

25 It should be noted that mixtures of organic surfactants can also be used in compositions of the present invention in order to achieve desired results.

30 It is known in the surfactant art, and especially in the detergent art, that additives called "builders" can be employed to increase the surfactant activity. In the case of detergents, the builders promote the detergent action and aid in solubility. Such builders can also be employed in compositions of the present invention. Inorganic materials, such as, alkali metal carbonates, phosphates, borates and silicates, are useful as builders. Such builders are quite useful with the sulphonic acid and sulphuric ester detergents and even with some of the nonionic types. Neutral reacting inorganic salts, such as, sodium sulphate and sodium chloride, also act as builders with these detergents. Organic builders can also be employed.

35 Illustrative examples are water-soluble, high-polymeric, gums, starches, and proteins. The sodium salt of carboxymethyl cellulose, methylcellulose, hydroxymethylcellulose, sodium polyacrylate, urea, thiourea, sodium citrate, sodium lactate, fatty acid

amides and alkylol amides, fatty acid nitriles and morpholides can also be used.

In the composition of the present invention the organosiloxane-oxyalkylene block copolymer is preferably present in an amount from 0.0001 to 1 weight per cent based on total weight of the aqueous solution. The weight ratio of the organosiloxane-oxyalkylene block copolymer to organic surfactant is from 0.001/1 to 99/1 in the novel compositions of the present invention. Preferably, the weight ratio of organosiloxane-oxyalkylene block copolymer to organic surfactant is from 0.05/1 to 1/1.

The mixture compositions of the present invention can be prepared in various ways. The organic surfactant and the organosiloxane-oxyalkylene block copolymer could first be mixed, and this mixture could be added to water whenever desired. An aqueous solution of the organic surfactant could alternatively be first prepared and then the block copolymer could be added to it. Still a further procedure would be to prepare an aqueous solution of block copolymer and then add the organic surfactant to it.

The compositions of the present invention may be used for example as detergents, emulsifiers, foamers, wetting agents, dispersing agents, flocculants and penetrants. Specific uses are as detergents and scouring agents in household and industrial cleaning application, car washes, rug and hair shampoos, bubble baths, upholstery cleaners, cosmetics, bottle washers, dentifrices and shaving soaps.

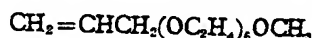
One use as a foamer is in the preparation of foams useful to entrain air in concrete and cinder block mixes to provide concrete, cinder blocks are preformed concrete slabs having reduced densities. Another such use is as foaming type flotation agents in metal ore separation and recovery systems. They are particularly useful in producing detergent foams of high stability and high foaming power in aqueous solutions. Other specific uses involve foam stabilisation and emulsification of water-organic solvent mixtures (such as water-toluene). Further utility may be found as a dye resistant, textile dye leveller, or dye dispersant.

The use of organo - silicon - oxyalkylene compounds to increase foaming power of a detergent is particularly novel and unobvious when compared to the prior use of organo-silicon compounds as antifoam agents.

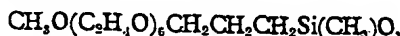
The present invention also provides an aqueous solution comprising essentially a composition as hereinbefore described and water. It is preferred that the organosiloxane-oxyalkylene block copolymer is present in an amount from 0.00001 to 75 weight per cent based on the total weight of the aqueous solution, and more preferably the organosiloxane-oxyalkylene block copolymer is present in an amount from 0.0001 to 1 weight

atoms, i.e., contains units represented by formula (1—a) described above, the addition process is preferable. If the metathesis process is used, many of the silicon-bonded hydrogen atoms will react with the alkali metal ions present in the reaction mixture.

When the copolymers useful in this invention contain olefinically unsaturated radicals attached to silicon, (for example, when R in formula (1) or (1—a) above is alkenyl or cycloalkenyl, such as vinyl or cyclohexenyl) it is preferable to prepare these copolymers by addition of the alkenyloxy-terminated oxyalkylene polymer to a monomeric, hydrolyzable silane containing silicon-bonded hydrogen, followed by cohydrolysis or co-condensation with other hydrolyzable silanes containing silicon-bonded hydrogen and silicon-bonded olefinically unsaturated hydrocarbon radicals using conventional techniques known to those versed in the art. For example, reaction of



with $\text{CH}_3\text{SiHCl}_2$ in the presence of a platinum catalyst followed by cohydrolysis of the product with $\text{CH}_2=\text{CHSi}(\text{CH}_3)_2\text{Cl}$, $\text{CH}_3\text{SiHCl}_2$, and $(\text{CH}_3)_3\text{SiCl}$ gives a copolymer useful in this invention containing units having the formulae



$\text{CH}_2=\text{CHSi}(\text{CH}_3)_2\text{O}$ and CH_3SiHO , terminated with $(\text{CH}_3)_3\text{SiO}$ groups.

Water-soluble organic surfactants or surface active agents which do not contain silicon and which are useful in the compositions of this invention can be conveniently classified as anionic, cationic, nonionic and amphoteric. These surface active agents are generally characterised structurally by an elongated non-polar portion having but little affinity for water or water-soluble systems and a short polar portion possessing high affinity for water and water-soluble systems. The non-polar portion is hydrophobic and the polar portion is hydrophilic.

If the elongated, non-polar portion of the molecule is included in the *anion* in the aqueous solution, the surfactant is called anionic. Sodium stearate is a typical anionic surface active agent which ionizes in water to form a sodium cation and the long-chain stearate anion which appears to be responsible for the surface activity. In the anionic class, the most commercially important anion groups are carboxy ($-\text{COOH}$), sulphonic acid ($-\text{SO}_3\text{H}$) and sulphuric ester ($-\text{OSO}_3\text{H}$).

The cationic or cation active surfactants ionize in water to form a *cation* containing the elongated non-polar portion. Cetylpyridinium chloride is an example. In the cationic class the most prevalent groups are primary, second-

ary and tertiary amino groups and the quaternary ammonium groups, Phosphonium and sulphonium groups are occasionally used.

The nonionic surface active agents do not dissociate in water but nevertheless are characterised by a relatively polar portion and a relatively non-polar portion. An example is N - (beta - hydroxyethyl)laurylamide.

The amphoteric surface active agents form zwitterions in water wherein a rearrangement occurs within the molecule so that the same molecule possesses both an anion and a cation. Cetylaminodiacetic acid is an example.

In the majority of surfactants useful in this invention, the long-chain non-polar portion of the molecule is derived from a straight-chain saturated hydrocarbon having from 8 to 24 carbon atoms. Generally, this long-chain portion is also a mixture of homologous radicals rather than a clearly defined individual radical. Thus, the molecule will generally contain a mixture of compounds ranging from C_8 to C_{24} but especially rich in the hydrocarbon for which the compound is named. The "lauryl" surfactants thus would be rich in C_{10} — C_{12} chains.

Illustrative examples of water-soluble surfactants useful in the compositions of the present invention are as follows.

Anionic surfactants can be carboxylic acids, such as, C_8 — C_{24} straight-chain saturated acids, oleyloxamic acid, N - dodecyl - N - hexylphthalamic acid; alkali metal salts of C_8 — C_{24} straight-chain saturated acids, such as, sodium stearate sodium laurate; alkali metal salts of oleic acid, such as, sodium oleate; alkane sulphonic acids and alkyl aromatic sulphonic acids, such as, dodecylbenzene sulphonic acid; esters of alkane sulphonic acids, such as, disodium-N-octadecyl-sulphosuccinamate, tetrasodium-N(1,2-dicarboxyethyl)-N-octadecylsulphosuccinate, diamyl ester of sodium sulphosuccinic acid, dihexyl ester of sodium sulphosuccinic acid, dioctyl ester of sodium sulphosuccinic acid, bis (tridecyl) ester of sodium sulphosuccinic acid, isopropyl naphthalene sodium sulphonate, dodecylbenzene sodium sulphonate, sodium dodecylidiphenyl oxide disulphonate, sodium dodecyl naphthalene sulphonate, ammonium tridecyl benzene sulphonate, amidomethylphenyl sulphonate, triethanolamine dodecylbenzene sulphonate, sodium lauryl sulphaacetate; alkali metal salts of substituted carboxylic acids, such as, sodium N - methyl - N - oleyl taurate, sodium lauroyl isothionate, sodium N - cyclohexyl - N - palmitoyl taurate, sodium N - methyl - N - palmitoyl taurate; sulphuric esters, such as, sodium teteradecyl sulphate, ammonium lauryl sulphate, diethanolamine lauryl sulphate, magnesium lauryl sulphate, potassium lauryl sulphate, triethanolamine lauryl sulphate, sodium lauryl sulphate, sodium lauryl ether sulphate, ammonium lauryl ether

TABLE

Surfactant Mixture (Parts by wt.)		Surface Tension in Dynes/cm. at 25°C. Concentration of Surfactant mixture (Wt. %)				Foam Height in mm. at 27°C. Concentration of Surfactant mixture (Wt. %)				*B— original from height. A— foam height after standing for 5 minutes			
Organic	Silicone	1%	0.1%	0.01%	0.001%	1%	0.1%	0.01%	0.001%	A	B	A	B
10	0	33.6	33.7	42.3	68.5	B*	A*	B	A	—	—	—	—
9	1	33.0	29.7	35.5	54.9	170	168	130	125	10	5	1	—
3	1	31.3	31.6	32.2	50.1	183	183	155	150	5	1	—	—
1	1	29.5	29.3	31.2	48.5	185	185	155	147	20	7	14	3
0	10	25.3	24.4	28.5	40.2	167	163	147	138	56	48	15	10
						141	125	85	75	43	36	19	14

It can be seen from the above table that the surface tension of the solution is desirably reduced as the organosiloxane-oxyalkylene block copolymer content increases. This becomes more pronounced at silicone surfactant mixture concentrations less than 0.1 wt. per cent. This in turn appreciably aids both the original foam height and also the stability of the foam upon standing when the solution is employed in foaming applications.

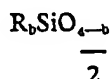
It can further be seen from the table that in the majority of cases the foam height and foam stability are substantially aided by the combination of organic surfactant and organosiloxane-oxyalkylene block copolymer according to the teaching of the present invention. Neither material alone will generally produce the desired results achieved by the novel combination.

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per cent based on total weight of the aqueous solution.

The present invention further provides a detergent composition capable of producing detergent foams of high stability in aqueous solution which consists essentially of (1) an organic detergent surfactant, (2) an organosiloxane - oxyalkylene block copolymer comprising (a) at least one siloxane block containing at least two siloxane units represented by the formula:



wherein R is a monovalent hydrocarbon radical, halogen-substituted monovalent hydrocarbon radical, or a divalent hydrocarbon radical and b is 1, 2 or 3, said siloxane block containing at least one of said siloxane units wherein at least one R radical is a divalent hydrocarbon radical, and (b) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R'O— , wherein R' is an alkylene radical, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon radical, the weight ratio of organo - siloxane-oxyalkylene block copolymer to organic detergent surfactant is preferably from 0.001/1 to 99/1.

The present invention also includes an aqueous solution capable of producing detergent foams of high stability which consists essentially of a detergent composition as described above and water, said solution preferably containing from 0.001 to 75 weight per cent of organosiloxane-oxyalkylene block copolymer based on the total weight of the solution.

The present invention will now be further described by way of example and by reference to the formula drawings accompanying the provisional specification, in which:—

Figs. 1 to 15 represent examples of

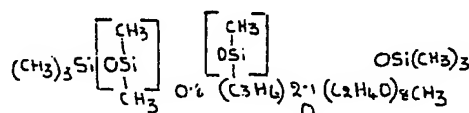
hydrolytically stable siloxane-oxyalkylene block copolymers which may be used in the compositions of the present invention. In these figures x is an integer. When the formula shown represents a unit of a polymer, it is to be understood that the polymer is terminated by chain-terminating groups of the type described above, and

Figs. 16, 17 and 18 represent examples of organosiloxane-oxyalkylene block copolymers which are especially useful in the compositions of the present invention.

The following Examples further illustrate the present invention without limiting it in any way.

EXAMPLE 1.

Aqueous solutions containing 1% by weight of sodium lauryl sulphate modified with different amounts of an organosiloxane-oxyalkylene block copolymer having the average formula



were prepared. Aliquot portions (50 ml.) of these solutions were diluted in 500 ml. graduated flasks to reduce the solution concentration by a factor of 10. This procedure was repeated using the weak solutions to obtain concentrations as low as 0.001% by weight. The surface tension of each solution was measured using the DuNouy Ring Method as described in ASTM—D—1331—54—T. The solutions were agitated and foam heights were measured at room temperature with the Ross Miles Foam Apparatus. This apparatus and method are described in detail in "Tergitol Surfactants" pages 30—31, published by Union Carbide Chemicals Company.

The results of these tests are shown in the following table.

Ross-Miles Foam Height
at Room Temperature (24–28°C) mms.

Surface Tension* at 25°C Dynes/Cm		% Concentration								Surfactants			
		1	0.1	0.01	0.001								
% Concentration		After 5 Mins.		After 5 Mins.		After 5 Mins.		After 5 Mins.					
1	0.1	0.01	0.001	Initial	Initial	Initial	Initial	Initial	Initial				
33.6	31.8	38.4	50.8	170	170	158	155	20	8	0	0	9	pts. sodium lauryl sulfate/1pt. Silicone surfactant ⁽¹⁾
33.5	31.0	27.6	43.4	177	175	154	151	31	15	0	0	6	” ” ” /1 ” ” ”
28.7	27.1	25.2	35.9	162	159	147	143	55	30	13	5	3	” ” ” /1 ” ” ”
25.6	24.0	23.0	27.6	163	160	143	143	47	40	11	7	1	” ” ” /1 ” ” ”
20.1	20.1	20.8	25.6	12	12	30	30	10	10	4	1	1	Silicone Surfactant ⁽¹⁾

*Surface tension measurements were determined by using a DuNouy Tensiometer.

$$(^1) \text{ Me}_8\text{Si}(\text{Me}_2\text{SiO})_9\text{OSiMe}_3\text{CH}_2(\text{C}_2\text{H}_4\text{O})_{12.9}\text{Me}$$

EXAMPLE 2
The procedure used in this example was results of this example are shown in the similar to that employed in example 1. The following tables: 5

TABLE II
Properties of Organic Surfactants with a Silicone Copolymer Additive

Ross-Miles Foam Height at Room Temperature (24—28 °C.)												
Surface Tension* at 25°C Dynes/Cm.		% Concentration										
		1		0.1		0.01		0.001				
% Concentration		After 5 Mins.		After 5 Mins.		After 5 Mins.		After 5 Mins.		Initial Mins.		
1	0.1	0.01	0.001	Initial Mins.	Initial Mins.	Initial Mins.	Initial Mins.	Initial Mins.	Initial Mins.	Initial Mins.	Initial Mins.	Surfactants
33.7	33.7	33.4	43.8	187	170	118	118	58	57	23	20	Nonyl phenyl polyethylene glycol ether
31.2	41.3	55.8	—	182	100	140	1	35	1	—	—	Sodium tetradecyl sulfate
33.6	33.7	42.3	68.5	170	168	130	125	10	5	1	0	Sodium lauryl sulfate
28.0	30.5	43.5	63.4	176	175	172	169	123	113	35	13	Sodium dodecyl sulfonate
25.9	28.1	41.5	56.3	192	178	158	135	93	0	28	0	Sodium di-octyl sulfosuccinate
25.3	24.4	28.5	40.2	141	125	85	75	43	36	19	14	Silicone surfactant ⁽¹⁾
28.9	29.0	31.3	43.0	185	160	115	95	54	48	20	15	9 pts. **Nonyl phenol polyethylene glycol ether/1 pt. ⁽¹⁾
27.5	27.3	35.2	63.3	176	95	130	5	38	8	20	7	9 „ Sodium tetradecyl sulfate
32.4	29.5	35.6	47.9	183	183	155	150	5	1	—	—	9 „ Lauryl sulfate
27.7	28.1	40.2	57.5	213	207	173	173	87	75	20	12	9 „ Sodium dodecyl sulfonate
26.7	25.8	40.4	55.1	193	180	165	145	79	50	22	14	9 „ Sodium di-octyl sulfosuccinate

*Surface tension measurements were determined by using a DuNouy Tensiometer.

**Parts by weight.

(1) $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{10-12}[\text{MeO}(\text{C}_2\text{H}_4\text{O})_{1-2}\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMeO}]_{1-1}\text{SiMe}_3$

TABLE V
Use of Combined Additives in Surface Tension Lowering
of Aqueous Surfactant Solutions

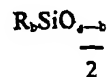
Major Component	Parts MM'(EO) ₂ CH ₃	Parts MD'M(EO) ₈ CH ₃	Surface Tension of Aqueous Solution	
			1.0%	Surfactant Conc. = 0.1% 0.01%
Sodium Lauryl Sulfate	0	0	32.7	31.9 44.5
"	0.5	0.5	26.5	27.0 29.1
"	0.25	0.75	27.4	27.2 28.3
C ₁₀ H ₁₈ O(EO) ₂₂ H	0	0	35.7	36.2 36.2
"	0.5	0.5	25.3	27.2 31.6

WHAT WE CLAIM IS:—

1. A composition for reducing the surface tension of an aqueous solution comprising an organosiloxane - oxyalkylene block copolymer together with an organic surfactant, said block copolymer comprising at least one oxy-alkylene block and at least one siloxane block said oxy-alkylene block containing at least two oxy-alkylene groups represented by the formula: 5 10

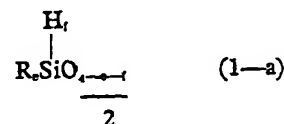


in which R' represents an alkylene radical, said siloxane block containing at least two siloxane units of the formula: 15



in which R is a monovalent hydrocarbon radical, a halogen substituted monovalent hydrocarbon radical or a divalent hydrocarbon radical and b is 1, 2 or 3, said siloxane block containing at least one said siloxane unit in which at least one R radical is a divalent hydrocarbon radical, said oxyalkylene and siloxane blocks being interconnected by said divalent hydrocarbon radicals. 20

2. A composition as claimed in claim 1 in which said siloxane block also comprises at least one siloxane unit of the formula:— 25



in which R has the meaning given in claim 1, e is 0, 1 or 2, f is 1 or 2 and (e+f) is 1, 2 or 3. 30

3. A composition as claimed in claim 1 or 2 in which the radical R contains at most 20 carbon atoms.

4. A composition as claimed in any of claims 1 to 3 in which said oxyalkylene block contains at least 4 of said oxyalkylene groups. 35

5. A composition as claimed in any of claims 1 to 4 in which R' contains from 2 to 10 carbon atoms.

6. A composition as claimed in claim 5 in which R' contains 2 or 3 carbon atoms. 40

7. A composition as claimed in any of the preceding claims in which said siloxane block contains a total of at least 5 siloxane units of the formulae 1 and 1a. 45

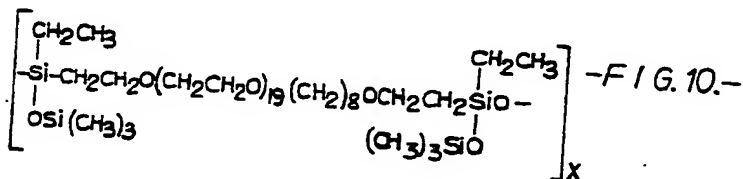
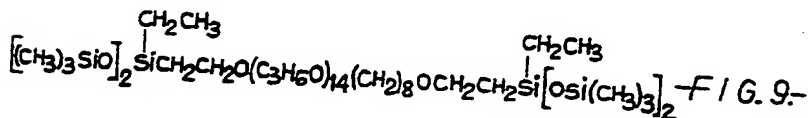
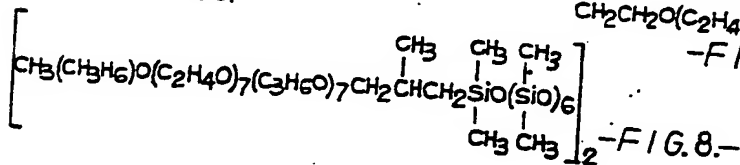
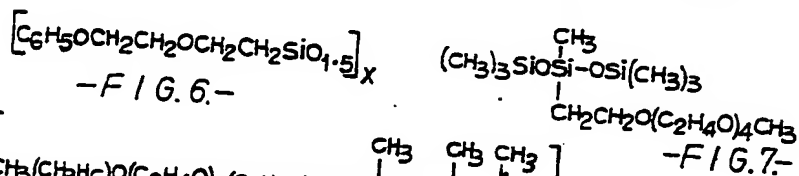
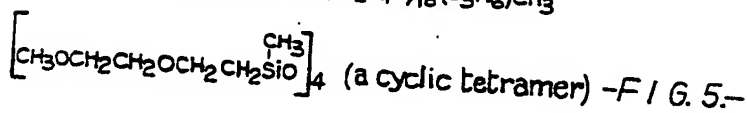
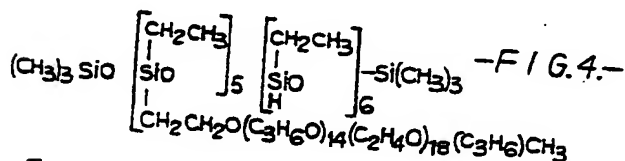
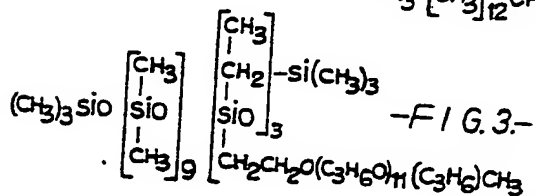
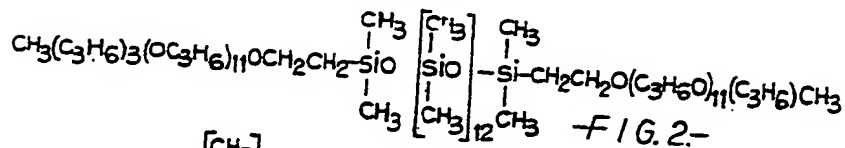
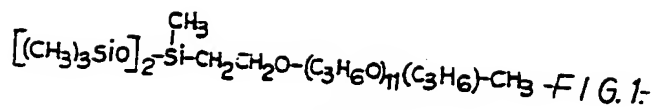
8. A composition as claimed in any of the preceding claims in which the portion of the average molecular weight of the block copolymer attributable to the siloxane blocks is at most 50,000. 50

9. A composition as claimed in any of the preceding claims in which the portion of the average molecular weight of the block copoly-

TABLE IV
Single Additives in Surface Tension Lowering
of Aqueous Surfactant Solutions

Additive*	Composition of Surfactant Mixture			Surface Tension of Aqueous Solution Dynes/cm.		
	Parts	Major Component	Parts Additive	1.0%	0.1%	0.01%
—	10	Sodium Lauryl Sulfate	0	32.7	31.9	44.5
MM'CH ₂ OCH ₂ H ₅	9	"	1	29.0	—	—
MM'CH ₂ O(EO)CH ₃	9	"	1	27.4	—	—
MM'(EO) ₂ CH ₃	9	"	1	26.0	28.6	41.9
MM'(EO) ₃ CH ₃	9	"	2	24.0	26.9	41.2
MM'(EO) ₄ CH ₃	9	"	1	27.3	—	—
MM'(EO) ₅ CH ₃	9	"	1	30.2	—	—
MD'M(EO) ₈ CH ₃	9	"	1	29.6	26.9	25.0
MD'M(EO) ₉ CH ₃	9	"	2	27.1	26.2	24.0
MD'M(EO) ₁₀ CH ₃	9	"	1	26.9	—	26.9
MD'M(EO) ₁₁ CH ₃	9	"	1	28.2	—	24.1
MD ₉ M'(EO) ₃ CH ₃	9	"	1	24.4	31.9	36.6
MD ₉ M'(EO) ₄ CH ₃	9	"	1	22.2	—	—
MD ₉ M'(EO) ₅ CH ₃	9	"	1	32.9	—	—
MD ₉ M'(EO) ₆ CH ₃	9	"	1	28.3	—	—
MD ₉ M'(EO) ₇ CH ₃	9	"	1	28.5	—	28.2
MD ₉ M'(EO) ₈ CH ₃	9	"	1	33.0	—	—

M = Me₃SiO, M' = Me₂SiOCH₂, D = Me₂SiO, D' = MeSiOCH₂, EO = C₂H₄O.



mer attributable to the oxyalkylene blocks is from 88 to 50,000.

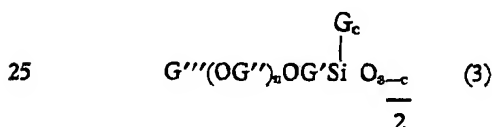
10. A composition as claimed in any of the preceding claims which contains from 0.001 to 99 parts by weight of block copolymer per part by weight of organic surfactant.

11. A composition as claimed in claim 10 which contains from 0.05 to 1 part by weight of block copolymer per part by weight of organic surfactant.

12. A composition as claimed in any of the preceding claims in which the block copolymer contains from 5 to 95 parts by weight of organo siloxane blocks and from 5 to 95 parts by weight of oxyalkylene blocks per 100 parts by weight of block copolymer.

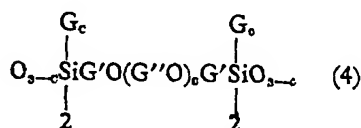
13. A composition as claimed in claim 12 in which the block copolymer contains from 5 to 50 parts by weight of organosiloxane blocks and from 50 to 95 parts by weight of oxyalkylene blocks.

14. A composition as claimed in any of the preceding claims in which the block copolymer comprises one or more units of the formula:



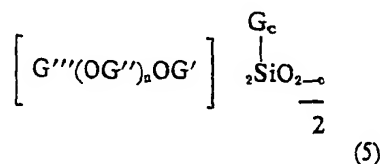
- in which G represents a monovalent hydrocarbon radical or halogenated hydrocarbon radical, G' represents a divalent hydrocarbon radical, G'' represents an alkylene radical of at least 2 carbon atoms, G''' is a hydrogen atom or a monovalent hydrocarbon radical free from aliphatic unsaturation, n is an integer of at least 2 and c is 0, 1 or 2.

15. A composition as claimed in any of claims 1 to 13 in which the copolymer contains one or more units of the formula



- in which G, G', G'', n and c have the meanings given in claim 14.

16. A composition as claimed in any of claims 1 to 13 in which the copolymer contains one or more units of the formula:



in which G, G', G'', G''' and n have the meaning given in claim 14 and c is 0 or 1.

17. A composition as claimed in any of claims 14 to 16 in which G contains at most 20 carbon atoms.

18. A composition as claimed in any of claims 14 to 17 in which G' contains at most 20 carbon atoms.

19. A composition as claimed in any of claims 14 to 18 in which G'' contains from 2 to 10 carbon atoms.

20. A composition as claimed in any of claims 14 or 16 to 19 in which G''' is a monovalent hydrocarbon radical free from aliphatic unsaturation containing at most 12 carbon atoms.

21. A composition as claimed in any of claims 14 to 20 in which n is an integer of from 2 to 30.

22. An aqueous solution of a composition as claimed in any of the preceding claims.

23. An aqueous solution as claimed in claim 22 in which said block copolymer is present in an amount of from 0.00001 to 75% by weight based on the total weight of the aqueous solution.

24. An aqueous solution as claimed in claim 23 in which the block copolymer is present in an amount of from 0.0001 to 1% by weight.

25. A composition for reducing the surface tension of an aqueous solution substantially as herein described with reference to Example 1.

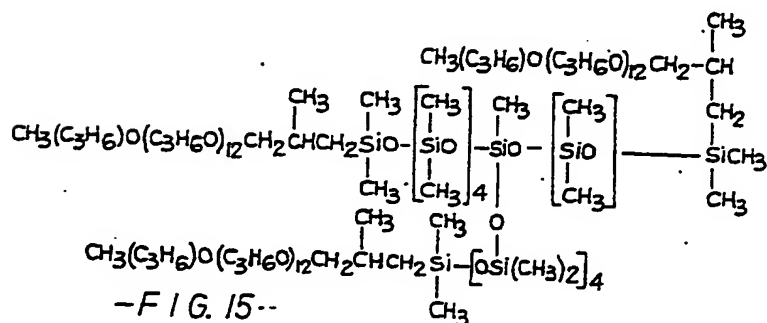
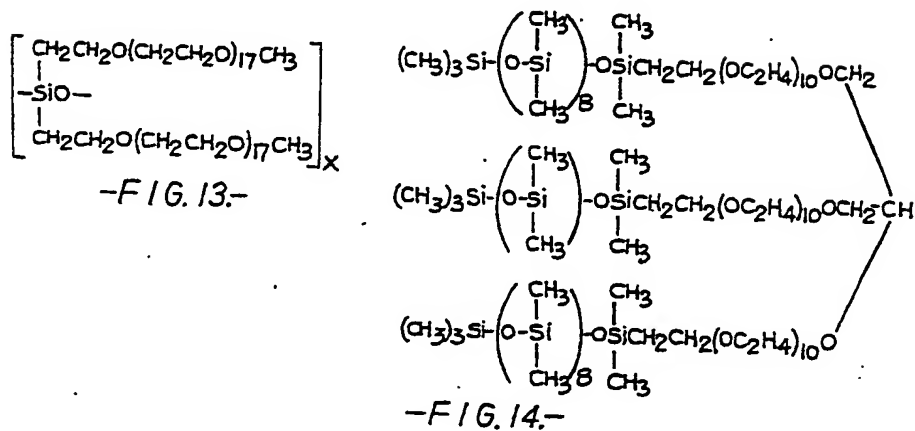
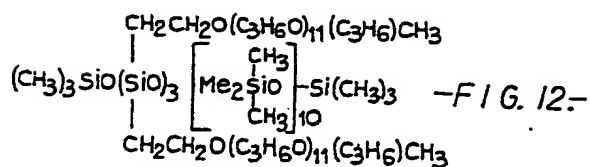
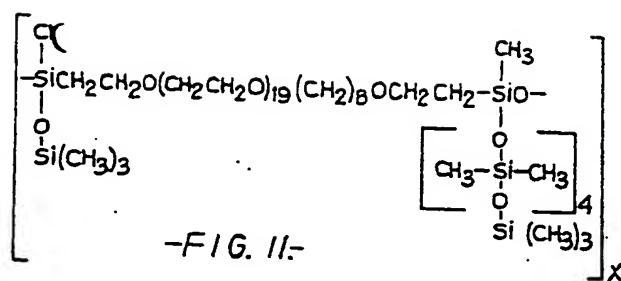
26. A composition for reducing the surface tension of an aqueous solution substantially as herein described with reference to Example 2.

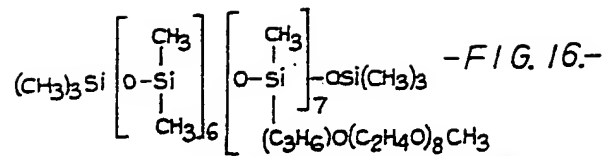
27. An aqueous solution substantially as hereinbefore described with reference to Example 1.

28. An Aqueous solution substantially as hereinbefore described with reference to Example 2.

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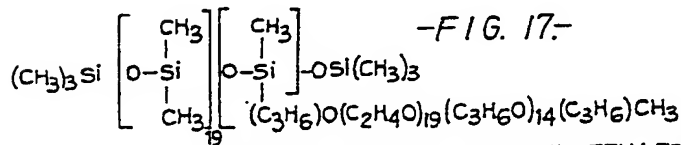
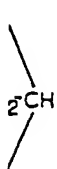
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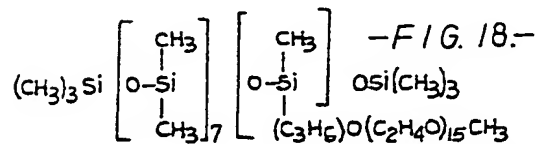


MOLECULAR WEIGHT OF APPROXIMATELY 3600

2



MOLECULAR WEIGHT OF APPROXIMATELY 7000



MOLECULAR WEIGHT OF APPROXIMATELY 3100